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RESULTS OF RESEARCH IN THE FIELD OF ALKYLPHENOL ADDITIVES

G. A. Zeinalova

Foreign Technology Division
Wright-Patterson Air Force Base, Ohio

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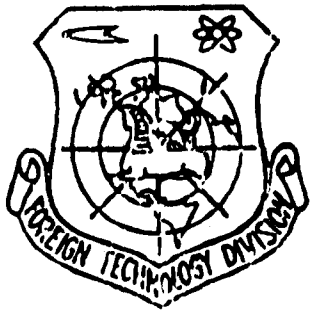
by

G. A. Zeynalova



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13. ABSTRACT

The prepn. of Ba and Ca salts of alkylphenols and bis(2-hydroxyphenylalkyl) sulfides, the condensation products of alkylphenols with HCHO or with HCHO and urea, an amine, or NH_3, the dithiophosphates of the latter, and the properties and performance of lubricating oils contg. these antiwear, antioxidant, anticorrosion, and detergent additives are reviewed with 24 refs. [AT1202028]

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	ROLE	WT	ROLE	WT	ROLE	WT
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Ammonia						
Sulfide						
Condensation Reaction						
Thiol						
Antioxidant Additive						
Anticorrosion Additive						
Detergent						
Lubricant Additive						
Formaldehyde						
Phenol						

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Б б	*Б б*	B, b	С с	*С с*	S, s
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О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

RESULTS OF RESEARCH IN THE FIELD OF ALKYLPHENOL ADDITIVES

G. A. Zeynalova

Alkylphenol additives hold a leading position among the numerous organic compounds used as additives for grease. Today in the Soviet Union and abroad many alkylphenol additives for various purposes are being produced [1].

Worldwide production and studies of the alkylphenol additives demonstrate that the most effective agent of the alkylphenol compounds are the alkylphenolates of alkali and alkali-earth metals.

The effectiveness of the alkylphenol additives can be explained by the fact that they as a substance of a basic character neutralize acids introduced into the fuel or which appear as a result of oxidation of the oil during engine operation; they are distinguished by high detergent and anticxidant properties.

The most extensive group of additives for multipurpose action which are in wide use, are the alkylphenolate sulfides.

Additives of the alkylphenol sulfide type can be divided into two main groups:

1) additives in which the sulfur atom is positioned between the aromatic rings;

2) additives which have the sulfur atoms on the alkyl radical.

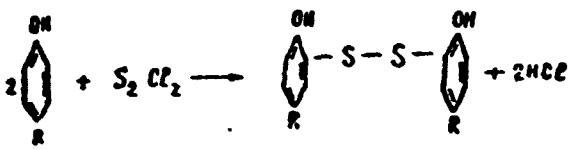
Additives in which the sulfur atom is located between the aromatic nuclei, basically have antioxidant and detergent properties.

Rather voluminous data on the synthesis of the above-mentioned additives can be found in the literature. These additives can be produced by the reaction of alkylphenols with chlorides of sulfur and the subsequent neutralization of alkylphenol sulfides with an oxide hydroxide of metals or with alcohols [1-4]. Sulfides and disulfides of alkylphenols which contain a sulfur atom between the aromatic nucleii are also used as anticorrosive additives.

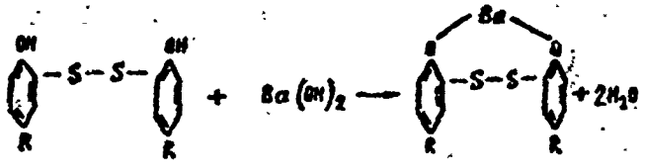
As is known, alkylphenol sulfide additives as TsIATIM-339, AzNII-TsIATIM-1, Paranox 56-A, and others belong to this type of additives.

The first alkylphenol additive produced for commercial use in 1950, was the AzNII-TsIATIM-1 additive which was developed by A. M. Kulneva, S. E. Kreyn, et al. [4, 5, 6].

The synthesis of the AzNII-TsIATIM additive consists of the following stages: a) production of alkylphenol by the alkylation of phenol with chloroparaffin; b) the treatment of alkylphenol with sulfur monochloride for the formation of alkylphenol sulfide;



c) the treatment of alkylphenol sulfide with barium hydroxide.



Also belonging to the same type of additive is TsIATIM-339 which is produced similarly except that the original alkylphenol is made by the alkylation of phenol using a polymer distillate [6].

Despite the fact that monosulfides and disulfides of alkylphenols are widely used on a commercial scale as additives for greases, they do not possess high anticorrosion properties. This can be explained by the three-dimensional effect of the alkyl and aryl groups. In aryl and alkylphenol sulfides the combining of the sulfur atom with the metals (i.e., the formation of a sulfide film) as a result of the screening by two bulky aryl radicals is made difficult, and thereby can lower the anticorrosion effect of the listed compounds.

The three-dimensional effect caused by the alkyl radicals, as compared with the aryl ones, is less, and therefore, the sulfur in alkyl sulfides, as compared with the sulfides of alkylphenols can more easily unite with metals in forming protective films. Therefore, the most effective anticorrosive additives made from organosulfur compounds turns out to be sulfides containing and aliphatic group on the sulfur atom.

Based on the foregoing, special interest is given to the synthesis and study of alkylphenol sulfide additives containing sulfur on a side alkyl chain. A multipurpose additive of the alkylphenol sulfide type containing sulfur on a side alkyl chain had been synthesized and was called AzNII-7 [7-8].

The synthesis of the mentioned additive consists of the following stages:

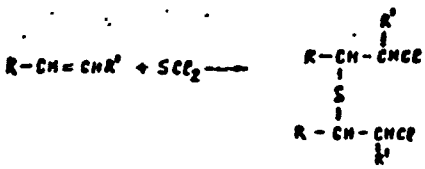
1) the production of the alkyl halide sulfides by the

interaction of unsaturated hydrocarbons with chlorides of sulfur;

2) alkylation of phenol with alkyl halide sulfides based on the Friedel-Crafts reaction;

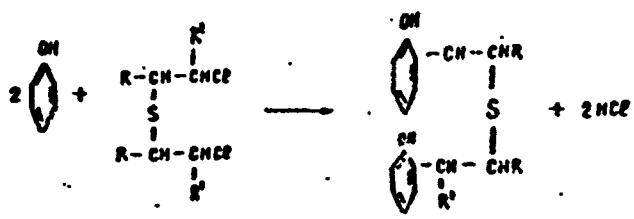
3) neutralization of the produced alkyl phenol sulfides.

We investigated the reactions of the unsaturated hydrocarbons produced by the thermal cracking of residual fuel oil with sulfur dichloride according to the following scheme:



The treatment of the fuel oil from the thermal cracking with sulfur dichloride was done at a temperature of 20-25°C for 3-4 hours; the amount of sulfur dichloride was about 15%, taking into account the fuel oil from the thermal cracking.

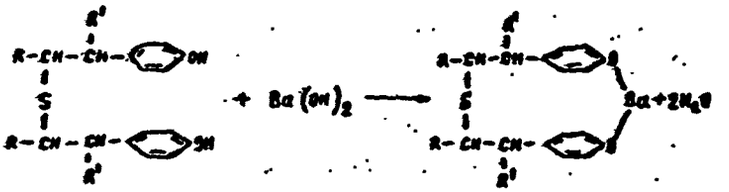
The second step in the synthesis of alkylphenol sulfide additive (AzNII-7 additive) included the alkylation of the phenol with alkyl halide sulfides according to the Friedel-Crafts reaction. Based on the data in the literature one can assume that the phenol is alkylated with alkyl halide sulfides according to the series of reactions:



The alkylation of the phenol can take place at a temperature of 85-90°C ober 4 hours in the presence of a 3% catalyst — aluminum chloride. The products of alkylation after the separation of the complex compounds is neutralized to a slightly alkaline reaction

with (2.5-3%) barium hydroxide at a temperature of 80-90°C. In order to remove the unused phenol and fuel oil from the thermal cracking, the product of alkylation is distilled up to a temperature of 160-165°C in a vacuum of 700-720 mm Hg. Under these conditions 30-35% of the products which did not enter the reaction are distilled off, and the remainder are alkylphenol sulfides having a viscosity equal to 12-13 cSt at 50°C.

The last step in producing AzNII-7 additive includes the neutralization of the produced alkylphenol sulfide with barium hydroxide:



The neutralization is done in "SU" machine oil at a temperature of 100-110°C.

The obtained AzNII-7 additive has the following properties: kinematic viscosity at 100°C – 8.76 cSt, ash content – 11.0%, barium content – 5.5-6.0%, sulfur – 3-4%, flash point – 120°C.

AzNII-7 additive is added to diesel oil of various grades at the rate of 3-5%. It has undergone comprehensive testing, beginning with laboratory investigations and ending with experimental use under field conditions. Numerous tests of the AzNII-7 additive under various conditions established that its addition to diesel oil effectively protects the engine parts from increased wear and harmful deposits during operation of fuels with a high content of sulfur.

By 1960 we developed the technology for producing the AzNII-7 alkylphenol sulfide at the city of Baku. During those years the output of motor oil with the AzNII-7 additive was a significant step forward in improving the performance of motor oils.

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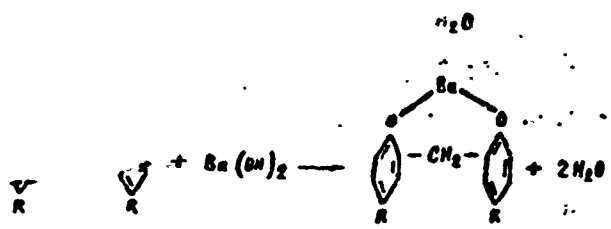


The conditions for producing the products of alkylphenol formaldehyde condensation were refined by working on the reaction of the individual alkhlphenols. Used as alkylphenols were p-tertiary butyl, amyl- and octylphenols. In order to produce the alkylphenol additive, the reaction of the condensation of the alkylphenols with formaldehyde is carried out as a molecular relationship at a temperature of 96-98°C in an acidic medium up to the stage of the formation of dialkyldioxy 5,5'-diphenyl methane.

As the result of the reaction of alkylphenols with formaldehyde a series of (5,5-dialkyl- 2,2-dioxy) diphenyl methanes should be produced whose physical constants would correspond to the theoretically calculated ones. The produced (5,5-dialkyl- 2,2-dioxy) diphenyl methanes were formed by barium hydroxide. The additive produced on a commercial alkylphenol base, was called BFK additive [9-12].

The conditions of condensation of the commercial alkylphenol with formaldehyde are analogous to those same individual alkylphenols. The synthesis of the BFK additive consists of the following steps:

1) production of the alkylphenol;

2) condensation of the alkylphenol with formaldehyde and the drying of the products of condensation;

3) saponification of the products of condensation with barium hydroxide;

4) separation of the sediments insoluble in benzene from the finished additive.

The commercial alkylphenol used for the synthesis of BFK is produced by the alkylation of phenol with a polymerdistillate in the presence of a benzene sulfonic acid or KU-2 as a catalyst.

At the end of the reaction the products of condensation are diluted with spindle oil at a ratio of 2:1, and allowed to stand for 3 hours. After the separation of most of the water the products of condensation are dried in a vacuum at a temperature of 100-110°C until their moisture content does not exceed 2-3%, after which they are saponified with 25% barium hydroxide at a temperature of 105-110°C. At the end of saponification the products of condensation are dried at a temperature of 110-115°C in a vacuum. The dried product undergoes centrifuging in order to separate the finished additive from the sediments insoluble in benzene. BFK additive has the following properties:

Ash content, %	9-10
Barium content, %	5-6
Alkalinity, mg KOH/g	55-60
D-11 oil +8% additive based on the stringent method at NAII, g/m^2	20-30

Detergent properties of D-11 oil +8% additive based on the TsZV method, points	0.5

BFK multipurpose additive in a mixture with oils from Baku and eastern sources at various concentrations were evaluated from the point of view of detergent, anticorrosive and antiwear properties. Results of the investigations confirmed that the proposed additive was extremely effective, and at concentrations of 6-8% exhibits significantly better detergent and antioxidant properties than AzNII-7 and TsIATII-339 commercial additives within acceptable concentrations. The indicated condition makes it possible to introduce subsequently a series of tests on BFK additive in a mixture with D-11 and DS-11 diesel oils in YaAZ-204 KDM-46, D-40, and 2D-100 engines, and a number of others under test stand and operating conditions.

Based on the favorable results of the tests obtained from the various engines BFK was authorized for use in industry.

An industrial plant for the production of BFK additive was built and put into operation in 1966 at planned full capacity.

The investigation of BFK additive at various levels of alkalinity indicated that its functional properties are significantly improved with an increase in alkalinity. Based on this deduction a high-alkaline additive, IKhP-101, was produced.

The synthesis of IKhP-101 additive is done by controlling the increase in its alkalinity and by increasing the degree of its purity. The increase in the degree of purity of the additive is attained by distilling off the residual fraction during the synthesis of the alkylphenol, and the increase in alkalinity – by a certain increase in the consumption of barium hydroxide. The technology of producing this additive is analogous to the technology of

producing BFK additive. Samples of IKhP-101 additive possess a higher degree of purity and better anticorrosive and neutralizing properties than BFK additive of conventional production. The analysis and preliminary laboratory tests of IKhP-101 additive are presented below:

Ash content, %	18-20
Total alkalinity, mg KOH/g	96-100
Detergent potential	98
Corrosion of D-11 oil +4% of the additive based on the stringent method at NAII, g/m^2	2-3
Detergent properties of D-11 oil +4% of the additive based on the method at PZV, points	0-0.5

The results of the preliminary laboratory and engine tests indicate that IKhP-101 additive at a 4% concentration surpasses the commercial BFK additive at an 8% concentration.

At the present time due to the lack of highly effective additives, oils of the IU series are being produced with an imported additive, Mobil'gard-593. Conducted research indicates the possibility of selecting compositions of the additives with a IKhP-101 base in order to produce the IU series of oil of group Ye. IKhP-101 was tested at the Lugansk diesel construction plant. Results of the test indicated that IKhP-101 additive makes it possible to produce the oil of group Ye which surpasses the imported sample of Mobil'gard-593 based on the effectiveness of reaction. At present more extensive tests of this additive are being run on various engines.

The attempt at producing and using the additives indicate that the alkylphenol additives consist of an effective synergic mixture with salts of carbonates and sulfonic acids.

Based on this the production of complex high-alkaline additives containing alkylphenol and acid radicals (carbonates and sulfonic acids) is of considerable interest.

A method for producing high-alkaline complex IKhP-136 additive was developed. The essence of this method includes the fact that sulfonic acid, alkylphenol and formaldehyde are condensed simultaneously and neutralized with a hydroxide of a metal. Taking into account that the reaction of phenol formaldehyde condensation is more sensitive in an acid medium than in an alkaline medium, alkylphenol formaldehyde condensation at first proceeds in the acid medium, and then the obtained product of alkylphenol formaldehyde condensation is saponified.

Serving as sulfonic acids, sulfonic acids produced by the sulfonation of diesel oil, were used and also calcium hydroxide was used as the hydroxide of a metal.

IKhP-136 additive has high neutralization numbers (on the order of 190-200 mg KOH/g) and effective operational properties. Oil of group Ye was used as a base for IKhP-136 additive, and was tested at the Lugansk diesel construction plant. The results of the tests indicated that the aforementioned sample of oil surpassed the foreign sample of Mobil'gard-593 based on the effectiveness of the reaction. At present more extensive testing of IKhP-136 additive is being run on various engines.

Considering the fact that barium hydroxide which is used in the production of BFK additive, is a scarce item, and that there is a circumstance where calcium salts are more effective in a number of additives, interest has been generated to investigate the possibility of producing additives of the BFK type, substituting calcium for barium (KFK additive).

The investigations we conducted indicated that it is not possible to produce the corresponding calcium salts as opposed to using barium salts (BFK) in the direct saponification of the products of alkylphenol formaldehyde condensation. Next, the additive was centrifuged in order to separate the sediments insoluble in benzene. The effectiveness of KFK additive at concentrations of 5, 8, 10% in a mixture with D-11 (Baku) diesel oil was investigated. The results of these tests indicated that KFK additive surpasses VNIINP-370 additive based on the anticorrosive properties, and ranks along side BFK additive based on this same index. The detergent and dispersing properties of an oil with KFK additive, as well as its resistance to oxidation as a thick layer at a high temperature (T_{250}) also puts this additive on the same level with BFK additive. The characteristics of KFK additive are presented below:

Ash content, %	5.2
Alkalinity, mg KOH/g	60.0
Detergent potential	62.0
Corrosion of D-11 oil +8% of the additive based on the stringent method at NAMI, g/m^2	12.0
Detergent properties of D-11 oil +8% of the additive based on the method at PZV, points	0.5

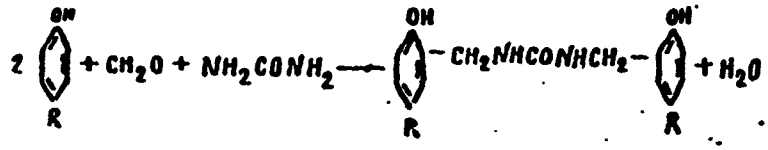
Besides the laboratory tests, tests of KFK additive were run on an engine. The test results of KFK additive in a mixture with D-11 oil on a YaAZ-204 engine over 600 hours indicated that this additive gives practically the same results as BFK additive, with the exception of the "piston ring wear" index whose absolute value is very low.

One of the important factors determining the operational qualities of oils is its resistance to oxidation by oxygen of the air.

In order to improve the antioxidant properties of lubricating oils we synthesized numerous nitrogen- and hydroxyl-containing compounds by reactions of alkylphenols with formaldehyde and various amines, and we investigated lubricating oils as antioxidant additives.

Nitrogen- and hydroxyl-containing compounds were produced by the condensation of alkylphenols with formaldehyde and carbamide, by the condensation of alkylphenols with formaldehyde and aromatic amines, and the condensation of alkylphenols with formaldehyde and ammonia. The condensation of the alkylphenols with formaldehyde and carbamide was done in a slightly acidic medium at a temperature of 96-98°C for 5 hours. Used for the reaction were alkylphenols of various lengths and various structured alkyl radicals.

A number of condensation products of alkylphenols with formaldehyde were synthesized whose physico-chemical constants agree with the theoretically calculated ones [13-16]:



The structure of the synthesized compounds was determined by spectral analysis and by subjecting them to the characteristic reaction for amines and hydroxyl containing compounds. The results of the investigations confirmed the suspected direction of the reaction of the condensation of alkylphenols with formaldehyde and carbamide.

The synthesized nitrogen- and hydroxyl containing compounds were investigated as antioxidant additives for energy oils. The investigations indicated that the synthesized compounds are effective antioxidant additives which improve the stability of the energy oils.

In order to conduct the extensive tests, combinations of this type with commercially-used alkylphenol. The obtained condensation product of commercial alkylphenol with formaldehyde and carbamide, called AzNII-11 additive, has the properties:

Additive	Molecular weight	Refractive index n_D^{20}	Density d_4^{20}	Viscosity at 100°C, cSt	Content, % N	OH
AzNII-11	520	1.5160-1.5180	0.9900-0.9950	100	3.2	7.0

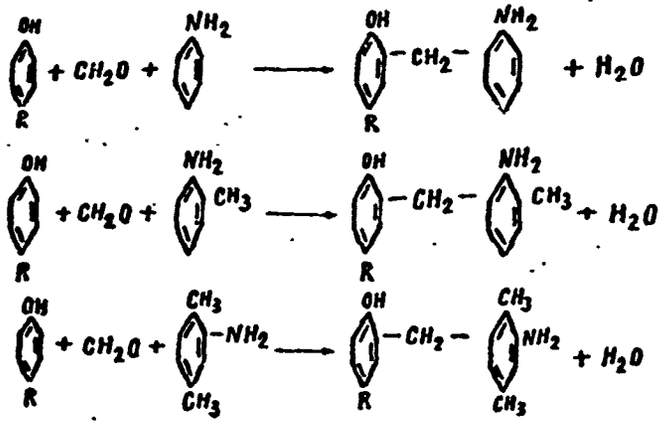
AzNII-11 additive was extensively tested as an antioxidant additive for energy oils. The test results of the oils – transformer and MK-8 with AzNII-11 based on the VTI method indicated that this additive by effectiveness is analogous to the existing antioxidant additives – Ionol and para-oxydiphenylamine.

Extremely interesting results were obtained from a comparison of the tested oils with AzNII-11 additive and Ionol under conditions of high oxidation temperatures. Thus, for example, at a temperature of 150°C Ionol did not affect the stability of MK-8 oil whereas AzNII-11 additive under these conditions of oxidation promotes a lowering of sedimentation and acid number of the oil.

The AzNII-11 additive in a mixture with transformer and turbine oils was also tested under operational conditions at the power stations of the State Trust for the Organization and Rationalization of Regional Electric Power Plants and Networks (ORGRES) (Moscow) and the Northern State Regional Electric Power Plant (GRES) (Baku). The results of these tests were favorable. Keeping in mind the high antioxidant properties of AzNII-11 additive, the uncomplicated technology of its production and the availability of the raw materials for its manufacture, the additive was recommended for use.

Antioxidant additives containing nitrogen and a hydroxyl group were also produced by the authors [17, 18, 19] by the condensation of alkylphenols with formaldehyde and aromatic amines. Analine, o-toluidine and p-xylidine were used as aromatic amines.

The condensation was conducted in a slightly alkaline medium at a temperature of 96-98°C for 3-4 hours. The products of the reaction after the separation of the reagents not consumed in the reaction were treated with dry hydrogen chloride, and the ammonium salts formed in this case were dissociated by an aqueous ammonia solution. A series of nitrogen and hydroxyl containing compounds with the following scheme of reactions was synthesized by the condensation of alkylphenols with formaldehyde and aromatic amines:



The physico-chemical constants of the synthesized compounds agree with the theoretically calculated ones.

The structure of the obtained compounds was determined by the infrared spectral method and by conducted chemical reactions characteristic for aromatic amines (with benzaldehyde, phthalic and acetic anhydrides). The results of the investigation confirmed the assumed direction of the reactions of the condensation of alkylphenols with formaldehyde and aromatic amines.

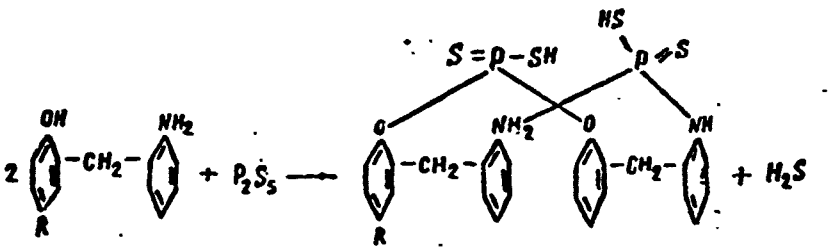
The effect of the condensation products of alkylphenols with formaldehyde and aromatic amines on the stability of D-11 and MK-8 oils was studied.

The conducted investigations indicated that the stated compounds suppress to a considerable degree the stability of the oils, and are equivalent to some of the existing antioxidant additives based on the effectiveness of the reaction.

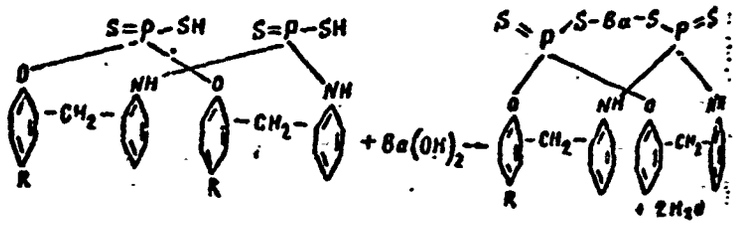
In recent years organic compounds containing sulfur and phosphorus – thiophosphate additives – have been extensively used as antioxidant and multipurpose additives for lubricating oils. A significant part of the thiophosphate additives belong to the type of salts of diethyl dithiophosphoric acids. We produced an antioxidant additive of that type of salt by treating the products of condensation of alkylphenol with formaldehyde and ammonia using phosphorus pentasulfide, and by treating the products of condensation of alkylphenol with formaldehyde and aniline, and by the subsequent neutralization of the obtained diethyl thiophosphoric acids with barium hydroxide (INKhP-21 and INKhP-25).

Antioxidant INKhP-25 additive is a barium salt of diethyl thiophosporic acids produced on a base of the condensation product of commercial alkylphenol with formaldehyde and aniline [20, 21].

The condensation of alkylphenol with formaldehyde and aniline is done in an alkaline medium at a temperature of 96-98°C in order to obtain the product with an refractive index of n_D^{20} = 1.5140-1.5160. The condensation product in a solution of spindle oil (a ratio of 2:1) is treated with 25% phosphorus pentasulfide at a temperature of 90-130°C. The assumed equation of the reaction is as follows:



The obtained diethyl dithiophosphoric acids are neutralized with 30-35% barium hydroxide at a temperature of 100-120°C according to the reaction:



The properties of the obtained INKhP-25 additive is given below:

Content, %	
Nitrogen	1.84
Phosphorus	3.4
Sulfur	6.64
Ash	20
Alkalinity, mg KOH/g	40
Corrosion of D-11 oil +1.2% of the additive based on the stringent NAMI method, g/m^2	0.8
Thermal stability of D-11 oil +1.2% of the additive based on the Papok method at 250°C, min	91

The investigation under laboratory conditions indicated that INKhP-25 additive is a multipurpose additive which improves the antioxidant and anticorrosive properties of the diesel oil.

A mixture of INKhP-25 and SK-3 sulfonate additive comprises the composition the additive. AS-10 oil with this composition was tested on a GAZ-51 engine. For comparison two standard samples were tested - AS-6 oil with 6% SK-3 and 1% DF-11, and AS-9.5 oil with 1.5% Monto-613 and 0.7% Santolyub-493.

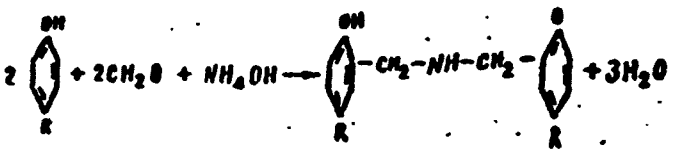
The test results indicated that the composition containing INKhP-25 and SK-3 based on its effectiveness to reduce wear of engine parts and to lessen the formation of deposits, surpasses the composition of additives from foreign firms, and that it ranks on the same level with compositions of SK-3 and DF-11 additives.

The high effectiveness of the composition of INKhP-25 additive with SK-3 was confirmed by the results of an operational test conducted at NIIAT on automobiles with ZID-164 and GAZ-51 engines, using this composition in a mixture with AS-6 oil.

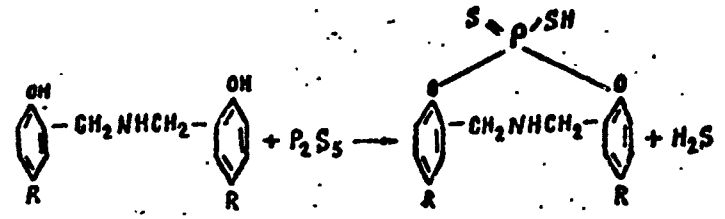
These test results indicated that the oil with the above-mentioned composition of additive facilitates the normal operation of the automobile engines.

INKhP-25 additive which includes sulfonate additive in its composition was authorized for use in carburetor engines.

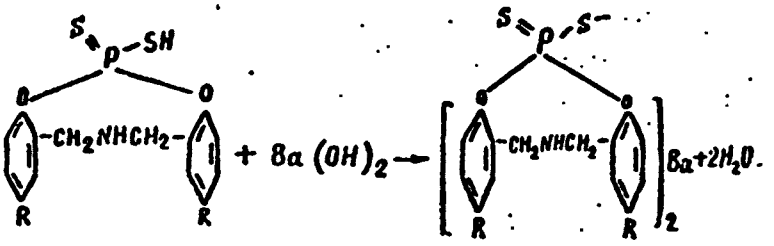
INKhP-25 additive is a barium salt of diethyl dithiophosphoric acids obtained as a base of a condensation product of commercial alkylphenol with formaldehyde and ammonia. The condensation of alkylphenol with formaldehyde and ammonia is done at a temperature of 96-98°C until a product is obtained with a refractive index n_D^{20} = 1.5140-1.5160. The assured scheme of the reaction is as follows [22, 23, 24]:



The condensation product of alkylphenol with formaldehyde and ammonia after preliminary treatment with spindle oil at a ratio of 2:1, is then treated with 25% phosphorus pentasulfide at a temperature of 90-130°C:



The neutralization of the diethyl dithiophosphoric acids was done with 35-40% barium hydroxide at a temperature of 120° according to the reaction:



The properties of the obtained INKhP-21 additive are presented below:

Content, %	
Nitrogen	1.8-2.0
Phosphorus	2.5-3.0
Sulfur	3.8-4.2
Ash	16-18
Corrosion of D-11 oil +1.2% of the additive based on the stringent NAMI method, g/m^2	0.2
Thermal stability based on Papok's method at a temperature of 250°C, min.	75

The results of the preliminary laboratory tests indicated that an oil containing INKhP-21 additive possesses high thermal stability, does not cause corrosion of lead plates during testing using the stringent NAMI method, and it is distinguished by relatively high

alkalinity. In addition, an oil with INKhP-21 additive does not cause corrosion of phosphor-bronze plates under oxidation in a DK-2 apparatus at a temperature of 200°C in the presence of an oxidation-naphthenate of copper catalyst.

For the purpose of explaining the possibility of using INKhP-21 additive in the composition of additives, its effect on the operational properties of oils containing SB-3, BFK and AzNIK-8u additives, was studied. The effect of INKhP-21 additive on the change in alkalinity of the oil with SB-3 detergent additive was studied at various heating temperatures. The results of the indicated tests showed that INKhP-21 additive owing to a sufficiently high thermal stability helps to maintain the alkalinity of the oil at a temperature of 300°C, whereas oils with antioxidant additives have a prevailing acid reaction already at a temperature of about 200°C.

The antioxidant effectiveness of INKhP-21 additive was studied under conducted motor tests on a GAZ-51 engine using AS-10 oil containing AzNII-8u additive; also tested was D-11 oil containing BFK additive, on a YaAZ-204 engine. The results of these tests indicated that when using INKhP-21 additive in almost all the evaluations significantly better results of engine performance ratings were obtained than when using other available antioxidant additives.

The investigations under laboratory conditions and during stand tests indicated that INKhP-21 additive possesses high antioxidant and anticorrosive properties and thermal stability which makes it possible to recommend it for use in the composition of alkylphenol and sulfonate additives in order to produce oils of the various groups.

Under laboratory conditions and at the experimental-industrial plant the final technology for producing INKhP-21 additive has been

refined, the material balance for the individual stages of synthesis has been formulated, and the necessary data for the planning of an industrial plant for the manufacture of INKhP-21 additive has been delivered. At the present time the plans for the industrial plant for the manufacture of INKhP-21 additive have been completed. Construction was scheduled to begin in 1970 at the plant for making the additives.

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